

## EVALUATION AND OPTIMIZATION OF TSNCO METHOD FOR HYDROXYL ANALYSIS

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## ABSTRACT

An analytical method for determining the hydroxyl content of hydroxyl-containing polymers was improved, optimized and evaluated for its applicability to a number of hydroxyl-containing materials. The method involves the reaction of the hydroxyl group with toluenesulfonyl isocyanate and subsequent acidimetric titration of the reaction product in a nonsqueous solution. The method is rapid, selective, yields reproducible results, and is widely applicable.

## INTRODUCTION

The accurate analysis of hydroxyl terminated polybutadiene (HTPB) and other hydroxyl-containing materials is a requirement which has become increasingly important in recent years in the aerospace industry. It is particularly significant in the area of propellant and liner technology utilizing any of the current hydroxyl/isocyanate systems.

The methods currently used most frequently for hydroxyl determination include acetylation, phthalation and reaction with p-toluenesulfonyl isocyanate (TSNCO). Acetylation and phthalation have been used for a number of years and have been fairly well-characterized. The TSNCO method, while faster and inherently more elegant, is relatively new and lacks a broad data base. The TSNCO method shows a great deal of promise, however, in that it is also more selective, more widely applicable, and capable of yielding better precision. In addition, the chemical reactions involved in the method closely approximate those of HTPB-isocyanate propellant systems.

The following report details a study which was undertaken to evaluate the TSNCO method on the basis of present experience and to improve and optimize the method where possible. In addition, the utilization of a recently purchased state-of-the-art automatic titration system was evaluated with respect to improving the accuracy and precision of the TSNCO method.

## OBJECTIVE

1. Evaluate the following parameters in the TSNCO method for hydroxyl analysis:
  - a. Blank Determination
  - b. Use of Catalyst
  - c. Reagent Stability
2. Incorporate the use of a recently purchased automated titration system in the determination of hydroxyl by TSNCO, with the aim of improving precision and extending the applicability of the method to a variety of materials.

## SUMMARY

1. Several significant improvements were made in the methodology of the TSNCO analysis:
  - a. In the course of the investigation, it was found that the use of a catalyst, which was previously assumed to be necessary to insure the quantitative reaction of TSNCO with HTPB, may apparently be eliminated altogether. This simplifies the method considerably, and removes one of the primary concerns with respect to variability.
  - b. State-of-the-art titration equipment eliminates the requirement to spike samples and blanks with an equal amount of a known hydroxyl compound. This was previously necessary because it is extremely difficult to visually resolve the two breaks in the blank titration curve when the spiking technique is not utilized. The ability of modern automatic titrators to electronically resolve the blank titration curve permits the elimination of the spiking procedure, thereby simplifying the method considerably and removing another potential source of variability.
  - c. State-of-the-art titration equipment yields improved precision because it results in more consistent endpoint interpretation, eliminating the variability introduced by individual operators in manually reducing the titration curve. Also, the new titrator extends the applicability of the TSNCO method to materials which yield much poorer titration curves than HTPB, since the instrument is capable of accurately resolving fairly poor breaks which would be extremely difficult to interpret manually.

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2. The stability of the TSNCO reagent was evaluated by observing the changes in a blank titration as a function of time and correlating these changes to the appearance of chemical species as predicted by the chemistry of the system. In addition, a method was devised to directly follow the isocyanate concentration of the reagent with time. It was found that the reagent is stable for approximately one week at ambient temperature in a closed container and for at least a month if kept refrigerated.

The tetrabutylammonium hydroxide titrant is reasonably stable for approximately one week at ambient conditions. After this time, some discoloration is usually observed. This solution is also stable for longer periods of time if kept refrigerated.

#### CONCLUSIONS AND RECOMMENDATIONS

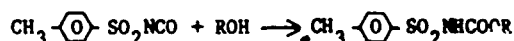
The revised TSNCO method generated by this investigation is simpler and less operator sensitive than the original procedure and appears to be generally applicable to nearly every type of hydroxyl-containing material encountered in this laboratory. It also yields excellent precision, with a one-sigma standard deviation of 0.00013 equivalents per 100 g for R-45M polymer. Since the accurate determination of hydroxyl content has traditionally been a problem area for HTPB and related materials, the revised TSNCO method holds a great deal of promise in the analysis of R-45M and other hydroxyl containing polymers used in the aerospace industry.

#### EQUIPMENT

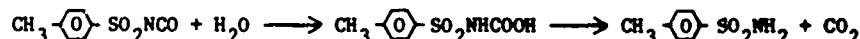
A Fisher Titrimeter II AEP automatic titrator was used to record the potentiometric titration curves and automatically determine the equivalence points. All chemicals were reagent grade and were used without further purification.

#### METHOD

The TSNCO method for the determination of hydroxyl content of HTPB and related materials depends on the reaction of the TSNCO with the hydroxyl-containing species to form a sulfonyl carbamate.

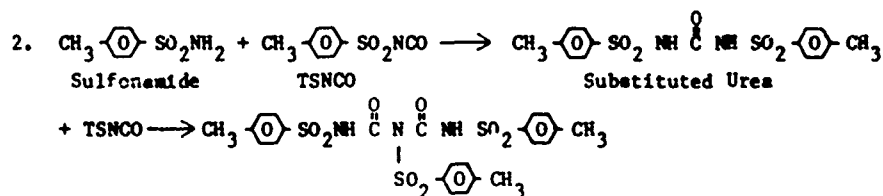
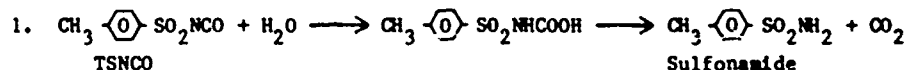


The sulfonyl carbamate is slightly acidic and can be titrated as an acid in certain nonaqueous media. The unreacted TSNCO is hydrolyzed with an excess of water, yielding p-toluenesulfonamide.



The sample dissolution, reaction and titration are carried out in tetrahydrofuran (THF). The reagent is a 0.2 N solution of TSNCO in THF, and the titrant is a standardized 0.1 N solution of tetrabutylammonium hydroxide (TBAH) in isopropanol. The titration is performed potentiometrically using a recording titrator with a combination glass electrode.

The titration curve obtained in this manner contains two distinct equivalence points. Figure 1 shows a typical sample titration curve for the analysis of R-45M by TSNCO. The first break is due to the presence of a small amount of a substituted biuret formed from the reaction of the sulfonamide with excess TSNCO:



The second break corresponds to the neutralization of the sulfonyl carbamate. The titration volume represented by the difference between the two breaks is a measure of the hydroxyl concentration.

A third equivalence point, found at a significantly larger titration volume, corresponds to the neutralization of the sulfonamide. P-toluenesulfonamide is slightly acidic under these conditions, and titrates as a weak monoprotic acid. This equivalence point has been largely ignored, since it does not enter into the calculation of hydroxyl content.

## TECHNICAL DISCUSSION

### 1. Blank Determination

One problem inherent in the TSNCO method involves the fact that the two breaks in the blank titration curve are sufficiently close together that visual resolution is extremely difficult (see Fig. 2). The blank titration volume cannot be ignored, however, since it is usually significant. Furthermore, the blank varies as a function of the vendor and lot number of TSNCO used, the age of the TSNCO solution, etc. The problem of determining the blank titration volume was originally resolved by adding a known amount of butanol to both sample and blank solutions. This spiking technique results in a sufficiently large separation of the two breaks in the blank titration curve that visual resolution is possible; the sample titration volume is then increased by exactly the same amount. While an accurate blank correction can be made in this manner, it represents an additional source of variability in terms of pipetting error, etc., as well as adding to the complexity of the method.

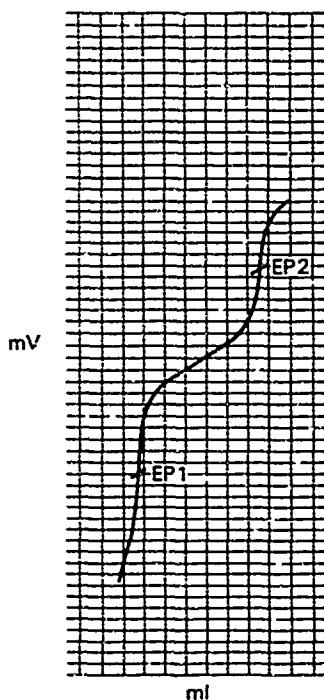


Figure 1. Sample Titration Curve.

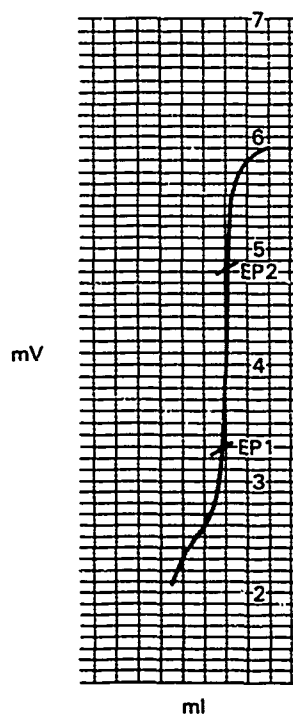


Figure 2. Blank Titration Curve.

The use of a new automatic endpoint-seeking titrator has several potentially significant implications with respect to the TSNCO method. The instrument, a Fisher Titrimeter II AEP system, is capable of electronically determining the equivalence point of a titration, thereby eliminating the requirement to manually reduce a potentiometric titration curve. Figure 2 shows a typical blank titration curve for a TSNCO analysis in which no butanol has been added. The actual blank volume in this case (EP2-EP1) is approximately 0.1 ml. While it is apparent that a visual resolution of this curve is difficult at best, the Fisher Titrimeter has no difficulty resolving both equivalence points at this degree of separation. In fact, resolution with as little as 0.02 ml difference was routinely achieved. The use of a state-of-the-art automatic titrator therefore obviates the necessity of spiking the blank and samples with butanol, thereby greatly simplifying the method and eliminating a potential source of variability.

### 2. Use of Catalyst

In the TSNCO method as it was previously written, the hydroxyl is reacted with isocyanate in the presence of a small amount of DBTDA catalyst. In practice, the sample solution is approximately 0.1 ml with respect to DBTDA. During the course of an interlaboratory evaluation of the method, several lab reported problems with certain lots of DBTDA. A catalyst evaluation was therefore undertaken to determine the effect, if any, of varying samples and lots of DBTDA reagent. In addition, it was decided to investigate alternative catalysts, notably triphenylbismuth (TPB). TPB was chosen because of its widespread use in current propellant systems.

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The results of the catalyst evaluation showed that a slight difference does exist between varying samples of DBTDA. The main difference involves the blank titration curve (Fig. 2). Certain lots of DBTDA cause a deterioration of the sharpness of the breaks in the blank curve to the extent that resolution of two separate equivalence points is no longer possible. This necessitates the spiking of blank and sample with a controlled quantity of alcohol to achieve resolution; the considerable advantage gained by using state-of-the-art titration equipment (see preceding section) is therefore negated. The detrimental effect of certain lots of DBTDA on the titration curve is probably due to reagent purity and/or degradation, since DBTDA can be purchased only as a technical grade material. However, no significant difference in the actual hydroxyl value obtained for a given lot of R-45M with differing samples was observed.

TPB was then evaluated as an alternative catalyst. It was found that TPB, at a 0.1 mM concentration, does not adversely affect the blank titration in any way. Excellent results were obtained using the Fischer Titrimeter without resorting to the spiking technique when TPB was utilized as the catalyst. It was noted, however, that THF solutions of TPB are not stable for long periods of time, as evidenced by the formation of a precipitate after a few days of standing at ambient conditions.

During the course of the investigation, a series of samples of R-45M were run without the use of a catalyst for comparative purposes. Somewhat surprisingly, it was noted that the R-45M samples run in the absence of any catalyst gave the same results as those obtained using either DBTDA or TPB. Table I summarizes the results for two lots of R-45M tested. This apparently contradicts the previously held assumption that a catalyst is required to insure quantitative reaction of the hydroxyl group with TSNCO. A number of other hydroxyl containing polymers were subsequently tested using the TSNCO method in the absence of any catalyst. Each of these samples was then analyzed by acetylation to provide a basis for comparison. In all cases, excellent agreement was obtained between the two methods. This indicates that, for all of the types of hydroxyl-containing polymers evaluated to this point, the use of a catalyst is apparently unnecessary.

TABLE II. HYDROXYL BY TSNCO ON VARYING R-45M SAMPLES

TABLE I. CATALYST STUDY, R-45M

Lot 6369 0009, 1% AO 2246	
Catalyst	Hydroxyl (eq/100 g)**
DBTDA*	0.0767
TPB*	0.0768
NONE	0.0768

\*0.1 mM solution  
\*\*Average of 3 determinations

Samples	Hydroxyl (eq/100g)
6369 0001	0.0784
6369-0008	0.0781
6369 0009	0.0767
6369 0010	0.0782
6369-0012	0.0799
6369 0013	0.0781
ARCO 309285	0.0792
ARCO 211125	0.0798
APCO 303065	0.0789
ARCO 229285	0.0789
6369-0007, 2% AO 2246	0.0790
6369-0007, Vanox 13	0.0790
6369-0007, Flexzone 6H	0.0810
6369-0012, Degraded	0.0792
8983-0003, No AO	0.0806
7842-0010, No AO	0.0829
210285, 3 days at 135°F	0.0799
6369-0007, Aged at 135°F	0.0776
6369-0008, With mid steel	0.0767

In order to further evaluate the revised TSNCO method as it applies to R-45M, a large number of samples of R-45M were collected from various sources throughout the laboratory and analyzed using the new procedure with the Fisher Titrimeter. No catalyst was used in any of these analyses. Samples included old lots of polymer, thermally degraded samples, AO-free materials, samples containing different types of AO, etc. Results are given in Table II. No problems were encountered with any of these varying samples, and precision was excellent in all cases. In addition, the possible effect of varying reactivity of the TSNCO reagent was checked by analyzing a given lot of R-45M (6369-0009) using each of the four different bottles of TSNCO which could be found in the lab at the present time. The results, as shown in Table III, indicate that all four lots of TSNCO reagent yield essentially identical data.

Several of the principal test parameters were evaluated in an effort to optimize these conditions with respect to the revised TSNCO method. Chief among the parameters evaluated were reaction time and sample size. R-45M was found to react quantitatively with TSNCO, in the absence of a catalyst, in less than 2 minutes. This was the minimum time in which reagents could be added, mixed, and the analysis initiated. For practical purposes, therefore, the reaction appears to be essentially instantaneous. In order to allow a large margin of safety, however, a reaction time of 3 to 5 minutes was specified in the procedure. Sample size was varied from 0.3 to 1.5 grams. At the lower values, very sharp breaks are obtained in the titration curve, but the volume of titrant added is sufficiently small that the

resultant relative error is large. Conversely, large samples yield satisfactory titration volumes at the expense of endpoint sharpness. Using the Fisher Titrimeter, a nominal sample size of approximately 1.0 g of R-45M constitutes an acceptable compromise.

In order to evaluate the precision of the revised TSNCO method, repetitive determinations were made on a sample of R-45M (Lot 6369-0009). Results, shown in Table IV, yield a one-sigma standard deviation of 0.00013 eq/100 g, or a relative standard deviation (RSD) of 0.17%. This compares to a one-sigma value of 0.00030 eq/100 g for the TSNCO method as previously written.

### 3. Reagent Stability

#### TSNCO REAGENT

In evaluating the stability of the TSNCO reagent (0.2 N solution of TSNCO in THF), two separate approaches were taken. In the first, reagent solutions were prepared from both a new and an old bottle of TSNCO. A portion of each of these two solutions was then kept in a sealed flask at ambient temperature, while the remainder was refrigerated in a sealed flask. A blank determination was run on each of these four reagent solutions at various time intervals over a one month period. Table V gives

TABLE IV. PRECISION STUDY

R-45M, LOT 6369 0009, 1% AO-2246

RUN NO	HYDROXYL (eq/100g)
1	0.0768
2	0.0768
3	0.0768
4	0.0768
5	0.0767
6	0.0767
7	0.0769
8	0.0765
9	0.0768
10	0.0768
11	0.0765
12	0.0768

AVE = 0.0767  
 $\sigma$  = 0.00013  
RSD = 0.17%

TABLE III. TSNCO REAGENT STUDY

R-45M, Lot 6369 0009, 1% AO 2246

TSNCO Lot	Hydroxyl (eq/100 g)*
Aldrich 2627LJ, Old	0.0768
Aldrich 2627LJ, New	0.0767
Aldrich 2814DH	0.0768
Kodak 711 1U	0.0767

\*Average of 3 determinations

the values for EP1, EP2 and the blank value (EP2-EP1) for each of these solutions as a function of time. The table shows that the ambient data are fairly consistent for approximately one week, after which the value of EP1 increases, indicating the probable decomposition of TSNCO via the urea/biuret reaction. The actual blank value (EP2-EP1) is also seen to increase somewhat at this time. For the refrigerated solutions, however, the data in Table I show virtually no change over a one month period. The data indicate little if any difference between solutions prepared from old and new lots of TSNCO under the same conditions. This experiment was then repeated for a TSNCO solution which was left in an open volumetric flask at ambient temperatures. The data, as given in Table VI, show a marked increase in the value of EP1 after one day, indicating a rapid decomposition of TSNCO under these conditions.

TABLE V. REAGENT STABILITY TITRATION VOLUME (ml) VS TIME

Time	Ambient						Refrigerated					
	Old TSNCO			New TSNCO			Old TSNCO			New TSNCO		
	EP1	EP2	Blank	EP1	EP2	Blank	EP1	EP2	Blank	EP1	EP2	Blank
0 Hours	1.16	1.24	0.08	1.11	1.19	0.08	1.14	1.22	0.08	1.11	1.19	0.08
4 Hours	1.16	1.24	0.08	1.25	1.33	0.08	1.20	1.28	0.08	1.19	1.27	0.08
12 Hours	1.36	1.49	0.13	1.34	1.47	0.13	1.25	1.36	0.11	1.38	1.48	0.10
1 Day	1.44	1.60	0.16	1.58	1.74	0.16	1.32	1.45	0.13	1.40	1.53	0.13
2 Days	1.40	1.55	0.15	1.51	1.66	0.15	1.42	1.54	0.12	1.47	1.59	0.12
4 Days	1.37	1.52	0.15	1.50	1.65	0.15	1.44	1.57	0.13	1.38	1.50	0.12
6 Days	1.47	1.53	0.16	1.62	1.82	0.20	1.38	1.50	0.14	1.36	1.50	0.14
12 Days	3.05	3.32	0.27	2.66	2.92	0.26	1.31	1.44	0.13	1.20	1.34	0.14
18 Days	4.09	4.39	0.30	3.12	3.42	0.30	1.28	1.42	0.14	1.20	1.34	0.14
30 Days	7.75	8.11	0.36	5.81	6.13	0.32	1.32	1.47	0.15	1.14	1.29	0.15

TABLE VI. REAGENT STABILITY, OPEN FLASK

Time	Titration Volume (ml)		
	EP1	EP2	Blank
0 Hours	0.45	0.47	0.02
4 Hours	0.70	0.75	0.05
1 Day	1.82	1.92	0.10
4 Days	7.34	7.44	0.10
7 Days	11.92	12.04	0.12

In addition to this approach, the actual isocyanate content of a TSNCO reagent solution under each of the above three conditions (ambient sealed, refrigerated sealed and ambient open to atmosphere) was monitored as a function of time. The isocyanate content was determined by treating an aliquot of the reagent solution with an excess of dibutylamine and back titrating potentiometrically with a standardized hydrochloric acid solution. The isocyanate content was then calculated as a percent of the original concentration. The results, as shown in Fig. 3, confirm the previous data in all three cases. A 0.2 N solution of TSNCO in THF appears to be stable for at least one month if sealed and refrigerated, for one week sealed at ambient, and for a maximum of one day if left open to the atmosphere at ambient conditions.

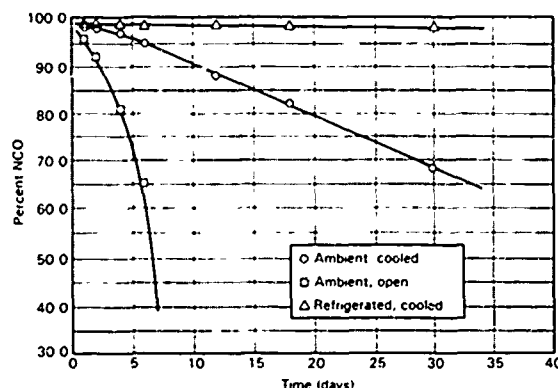


Figure 3. Reagent Stability vs. Time.

#### TBAH TITRANT

Much more information is available regarding the stability of TBAH solutions than for TSNCO solutions. A 0.1 N solution in isopropanol is known to decompose slowly at ambient temperature; this is visually evident in the form of a yellow discoloration which forms after approximately 3 to 4 days. The titrant was found to maintain a fairly stable concentration even after the appearance of the yellow color, however. Nevertheless, it is recommended that a 0.1 N solution of TBAH be discarded after approximately one week at ambient conditions. It is also recommended that the standardization of the titrant solution be checked approximately every two days. If the titrant is used past the point of initial decomposition, serious problems can be encountered. One of the decomposition products of the quaternary ammonium hydroxide solutions is the corresponding alkyl amine, which itself is quite basic and readily reacts with acidic species. The result is a nonstoichiometric situation which cannot be corrected. For this reason, TBAH titrant solutions should not be used long after initial decomposition is observed.

It was also found that 0.1 N solutions of TBAH in isopropanol could be kept for considerably longer periods of time if the solution is refrigerated. Sealed, refrigerated titrant solutions were found to maintain a constant titer without any visible signs of discoloration for as long as four weeks. Owing to the considerable cost of the TBAH reagent, refrigeration of stored titrant solutions is a practical means of extending the lifetime of a fairly expensive reagent solution.